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Ionization and dissociation of H_2, N_2 and CO in charge exchange collisions with positive ions

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With 1 figure in the text

ABSTRACT

A double mass spectrometer has been constructed which permits the measurement of charge exchange cross sections for collisions between molecules and ions with kinetic energies between 900 and 25 eV. Mass spectra of the collision products are obtained. H_2, N_2, and CO have been bombarded with 15 different atomic ions and the cross sections for the production of H_2^+, H^+, N_2^+, N^+, CO^+, C^+, and O^+ have been determined as a function of the ion kinetic energy. The processes in the collision chamber are discussed in terms of the known recombination energies of the atomic ions and the appearance potentials of the molecular fragments investigated.

Introduction

In earlier papers [1, 2, 3, 4, 5] Lindholm has investigated collisions between molecules and atomic ions using mass spectrometrical analysis of the collision products. The experiments were performed with a 500 eV kinetic energy of the incident ions, since, if the kinetic energy was varied by application of retarding electrical fields, such strong de-focusing of the ion beam appeared that cross-section measurements became impossible.

These difficulties have been eliminated with a new apparatus and the collision cross-sections may now be determined as a function of the kinetic energy between 900 eV and 25 eV; resulting in highly improved possibilities to interprete our measurements. In several theoretical and experimental investigations [6, 7, 8, 9, 10, 11], the dependence of the charge exchange cross-section on the kinetic energy of the incident ion has been discussed. The result is that the variation of the cross-section with kinetic energy depends mainly upon the energy change, ΔE, in the internal motion in the collision. If this energy change, ΔE, is very small, the cross-section is large for small kinetic energies and falls as the kinetic energy increases. We then say that the cross-section curve has *resonance form*. If, on the other hand, the energy change, ΔE, is great (positive or negative) the cross-section increases to a maximum and then falls. The location of the maximum has been investigated by Hasted and co-workers [11] and it may now be estimated by means of their diagrams. In this case we say that the curve has *defect form*.

To be able to discuss the energy difference, ΔE, which is simply the difference of the ionization energies, Lindholm has instead used the notation recombination energy (RE) for the incident ions and appearance potential (AP) for the fragments of the molecule.

Apparatus

The new apparatus is placed inside a large vacuum container with diameter 1300 mm and height 1100 mm. The container is evacuated with a large oil-diffusion pump having a pumping speed of 5000 l/s. Between the oil-diffusion pump and the container we have a water-cooled baffle and a valve with diameter 400 mm. The vacuum in the mass spectrometer magnets is very good even though large quantities of gas are introduced into the ion source and the collision chamber. Further, there is no risk of diffusion of gas from the ion source to the collision chamber.

The atomic ions (called A) are produced in an ion source of Heil type and are analyzed in a semicircular, inhomogeneous, permanent magnet A with radius 180 mm. The kinetic energy of the ions is then between 2000 eV and 3000 eV. After the analysis, the atomic ions are retarded in a system of electrostatic lenses down to the desired kinetic energy. The electrodes are given potentials such that the ion beam is focused on the entrance slit of the collision chamber after the retardation.

The collision chamber is filled with the gas to be investigated; H_2, N_2, or CO, to a pressure of 1.7×10^{-4} mm Hg. The pressure is measured by means of a glass Knudsen gauge [12]. Thus it is possible to obtain a satisfactory evacuation of the gauge through the narrow slits in the collision chamber. After having passed the collision chamber, the atomic ions, A, are collected in a collector and are measured by means of electrometer tube amplifier, A, which is at approximately the same potential as the collision chamber and therefore must be very well insulated. The ion beams A usually amount to between 10^{-8} amp and 10^{-11} amp and therefore a resistor of 10^8 ohms is used.

In the collision chamber ionized fragments (called B) are obtained from the gas molecules. The ions B are extracted towards one side of the collision chamber by a weak repelling voltage, are accelerated, and are analysed in a permanent magnet B of the same kind as magnet A but with radius 250 mm, and are finally collected and measured with a vibrating reed electrometer B, which is grounded. The accelerating voltage is fixed at 4800 V, therefore the magnetic field has to be varied. This variation is performed by shunting the magnet with iron, and can easily be done using a shaft through the wall of the vacuum container. The ion beam B is normally between 10^{-11} amp and 10^{-15} amp and therefore a resistor of 10^{11} ohms is used.

To avoid surface charges all surfaces have been coated with colloidal graphite in alcohol [13].

In order to check and calibrate the apparatus the collisions of He^+, Ne^+, Ar^+, and Kr^+ in their own gases were investigated with the above mentioned pressure in the collision chamber. If the ion beams A and B are measured in volts, corresponding to the resistances mentioned above, and if Q designates the cross-section, we obtain $Q = K \cdot (B/A)$ where K is a constant. The unit Å^2 for the cross-section means 10^{-16} cm^2 and corresponds to $1.13\,\pi a_0^2$ or to 3.29 cm^{-1}, i.e. cm^2/cm^3 at 1 mm pressure and 20°C. By comparison with absolute determinations of Q, the constant K can be determined. If the measurement is then repeated with other ions and other gases, the constant K ought to be unchanged provided the pressure in the collision chamber and the resistors are unchanged and that the extraction of the ions B out of the collision chamber is constant. This probably is the case if the magnetic field B is varied and the accelerating voltage during the analysis in magnet B is fixed.

The results of the experiments with the noble gases, for some kinetic energies, are shown in Table 1 which gives the collision cross-sections obtained during this work and also during some earlier absolute determinations that were made without magnetic analysis of the collision products. The constant K was chosen in such a way that for argon at 400 eV our cross-sections agree with the measurements by Hasted [10]. The Table shows that the agreement between our measurements and the earlier absolute measurements must be considered satisfactory in the following two respects. First there is agreement as to the variation of the cross-section with the kinetic energy and secondly there is agreement not only for argon but also for all other gases. This means that the constant K seems to be independent of the mass of ion B. We can therefore assume that all measurements with different fragments are characterized by the same K-value. Because of the complicated ion paths and the slits in mass spectrometer B, this good agreement was somewhat unexpected.

The sources of error that can influence the K-value depend on the ion paths in the collision chamber. If the ion beam A is diverging in the collision chamber so that it is not completely collected by collector A, or if ion beam A does not pass exactly in front of the slit in the collision chamber, through which ion beam B leaves the chamber, we obtain erroneous results. The latter difficulty now seems to be most important owing to the effect of surface charges. All these different sources of error can now to a certain degree be checked in the following manner.

The retarding electrostatic lens system is in two parts. The first part consists of two narrow slits placed immediately after each other. Between these slits there is a retardation to one of the energies: 1000 eV, 750 eV, 500 eV, 375 eV, 250 eV, or 187 eV. The ion beam A then enters the second part which consists of 10 electrodes after each other with different potentials. In this second part there is further retardation so that the kinetic energy of the ion beam decreases to 0.9, 0.3, 0.1, or 0.03 of the above-mentioned energies.

Fig. 1 shows a curve corresponding to the uppermost line in Table 1. It thus indicates the cross-sections for Ar^+ in Ar that were measured on one occasion. The curve consists of four parts. The first part goes from 900 eV to 168 eV and corresponds to

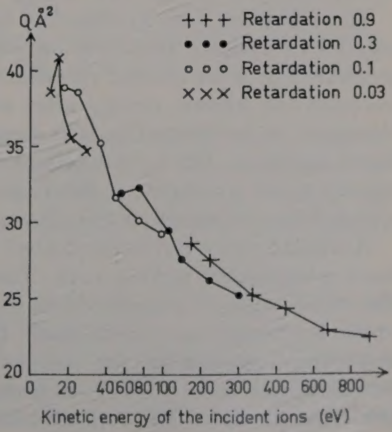

Fig. 1. Charge exchange cross-sections Q for Ar^+ in Ar corresponding to the first line in Table 1.

Table 1. Calibration of apparatus by means of charge exchange in noble gases with known cross-sections Q.

Process	$Q_{25\,V}$ Å²	$Q_{50\,V}$ Å²	$Q_{150\,V}$ Å²	$Q_{400\,V}$ Å²	$Q_{900\,V}$ Å²	Author
$Ar^+ \rightarrow Ar$	38	34	29	25	23	Present experiment
	39	36	30	25	22	Hasted [10]
		35	30	25	21	Dillon *et al.* [14]
			23	22	22	Ghosh-Sheridan [15]
	30	25	23			Potter [16]
	25	25	39	39	34	Gilbody-Hasted [11]
$Kr^+ \rightarrow Kr$		36	32	30	26	Present experiment
		46	38	32	28	Dillon *et al.* [14]
			34	31	31	Ghosh-Sheridan [15]
$Ne^+ \rightarrow Ne$	26	23	18	16	14	Present experiment
		19	16	12	11	Dillon *et al.* [14]
			17	15	15	Ghosh-Sheridan [15]
	11	11	17	16	14	Gilbody-Hasted [11]
$He^+ \rightarrow He$	27	16	13	11	9	Present experiment
	12	11	10	8	7	Hasted [10]
			11	9	8	Stedeford-Hasted [17]
	16	15	14	13	12	Gilbody-Hasted [11]
		14	10	9	8	Dillon *et al.* [14]
			13	12	12	Ghosh-Sheridan [15]
	13	12	11			Potter [16]

the retardation 0.9. The second, corresponding to the retardation 0.3 goes from 300 eV to 56 eV. The third goes from 100 eV to 18.7 eV. The fourth part, corresponding to the retardation 0.03, begins at 30 eV but cannot be continued further than to 11.2 eV owing to the diminished intensity of ion beam A. Each of these four curves is characterized by different ion paths in the retarding lenses and in the collision chamber. Therefore errors usually can be detected if the different parts do not overlap sufficiently. It is surprising that the curve could be followed down to so low an energy as 11 eV. Of course no importance can be given to these values for lack of absolute determinations of Q in this energy range.

The retarding lens system has been separated in two parts as the computations seemed to indicate that it is impossible to construct a single electrostatic retarding positive lens with greater retardation than 0.03, where this number gives the ratio between the kinetic energy after and before the retardation. The retardation must therefore be performed in two steps. In the first step the angular spread of the ion beam increases, but as the slits are narrow and placed at the crossover of the beam, this does not constitute a disadvantage. The second step functions as a positive lens which forms an image of the slits on the entrance slit of the collision chamber.

A similar curve has been plotted for each of the fragmentation processes that have been investigated in this work. The deviations of the measured values have been of the same order of magnitude as in Fig. 1, except in some cases when the intensities of the ion beams have been small. It thus seems probable that the form of the curves is accurate enough for the conclusions drawn from the form of the curves. It has, however, not been possible to obtain the same accuracy for the absolute values of the cross-sections. The reproducibility of the measurements shows that some measured values are probably impaired with an error amounting to a factor 1.5 or possibly more. If, on the other hand, we compare with the absolute measurements that have been performed by other authors, we find in most cases an astonishingly good agreement; but in some dissociation processes the earlier absolute measurements indicate greater cross-sections than ours (see Table 5: He^+ and Ne^+).

The recombination energies (RE) of the incident ions

The RE for the incident ions have been tabulated [3], and later discussed [4, 5] by Lindholm.

The importance of these RE for the collision processes is related to the abundance of the corresponding ion state in the ion beam. We must imagine that the ions are formed in the ion source in several excited states. During the time necessary for the ion beam to pass from the ion source through magnet A to the collision chamber the ion may emit radiation and make a transition to the ground state or to one of its metastable states. As this time amounts to about 10^{-6} seconds [18], the states with a lifetime amounting to at least 10^{-6} seconds, must be considered as metastable in this connection.

For some ions the lifetimes of the metastable states have been computed theoretically [19, 20] but for most ions there are no computations, and we must therefore use the spectroscopic selection rules or may in some cases estimate the lifetime of the state from the intensity of the corresponding spectral lines. It seems therefore to be of interest to try to experimentally measure the abundance of different metastable states in the ion beam. Very few such investigations have been performed. Hagstrum [21] has observed metastable states in ion beams of Ar^+, Kr^+, and Xe^+.

Lindholm's investigations have shown that usually all low metastable states of the ion are represented in the ion beam. In the present work further observations have been made regarding the following ions.

Ar^{++} and Kr^{++}: von Koch and Lindholm [22] have shown that in collisions with C_2H_5OH the effective RE of Ar^{++} seem to amount to about 24 and 11 eV. For Kr^{++} they seem to be approximately 21 and 11 eV. From this it follows that the conclusions that Lindholm [3, 4, 5] draws from the cross-sections with doubly charged ions cannot be maintained.

F^+: The existence of RE 20.01 has with certainty been proved in the process $F^+ + H_2 \rightarrow H^+$. Here H^+ is formed to a relatively great extent and the cross-section curve has resonance form. Further, RE 17.42 has been observed in the process $F^+ + H_2 \rightarrow H_2^+$.

Ar^+: Lindholm [3] has discussed the possibility that there might exist a RE in the range 17.86–20.41, corresponding to the metastable ions later observed by Hagstrum (21). Perhaps this possibility explains the cross-sections obtained in the process $Ar^+ + H_2 \rightarrow H^+$. It is interesting that the cross-section curve has a maximum at 150 eV.

N^+: This ion may exist in four states with the following RE: ^3P: 10.97, 12.16, and 14.54 eV. ^1D: 12.87, and 14.06 eV. ^1S: 15.03 eV. ^5S: 20.34 eV.

In the process $N^+ + CO \rightarrow CO^+$ the cross-section increases with increasing kinetic energy (see Table 6). It is therefore probable that RE 14.06 is of small importance in the ion beam. This is especially evident when comparing with Kr^+, which has approximately the same RE (14.00), but where the cross-section curve for the process $Kr^+ + CO \rightarrow CO^+$ has resonance form. We thus find that the ^1D state of N^+ with RE 12.87 and 14.06 is present in only small quantities in the ion beam. — Hasted [23] has found that in the process $N^+ + Kr \rightarrow Kr^+$ the cross-section has resonance form. He interpreted this as a proof that RE 14.06 is of importance. It seems, however, possible that the curve form could have been explained equally well by means of RE 14.54 for N^+ and AP 14.67 for Kr^+.

In the process $N^+ + H_2 \rightarrow H^+$ the cross-sections are very small. This must mean that the ^5S state with RE 20.39 is absent in the ion beam (see Table 3), as has already been pointed out by Lindholm [3], and it is especially evident when comparing with the process $F^+ + H_2 \rightarrow H^+$, in which case the cross-sections are large owing to RE 20.01 for F^+.

We thus find that the ^3P state is of importance in the ion beam and that the importance of the ^1S state is unknown. It is interesting to note that Frost and McDowell [24] and Fineman and Petrocelli [25, 26] have found that when N_2 is bombarded with electrons of energy less than 30 eV, N^+ is formed exclusively in the ground state ^3P. Further, Lindholm [3, 4, 5] could not observe any difference between N^+ ions of different origin (from N_2, N_2O, and NH_3).

The process $N^+ + CO \rightarrow O^+$ is, according to Table 7, characterized by larger cross-sections than the other processes in this Table. Also the cross-section in the process $N^+ + N_2 \rightarrow N^+$ is remarkably large. As the RE for N^+ is lower than 15.03 eV, both observations are impossible to explain by means of this RE. A possible explanation is that the ion beam contains N_2^{++} ions whose RE are of the order of magnitude 35 eV [27, 28]. That N_2^{++} is of importance in the ion beam from N_2 is apparent from the ionization efficiency curve by Hagstrum and Tate [28] and from measurements by Dibeler, Mohler and Reese [29].

H^+: RE 13.60.

O^+: Lindholm has earlier observed that O^+ ions from CO, N_2O, and CO_2 have different properties. The present measurements make it possible to discuss this in more detail. In the process $O^+ + H_2 \rightarrow H^+$ the curve has resonance form. This proves the existence in all three beams of ions in the ^2P state that is responsible for the RE 18.64. In ion beams from CO_2 this ion state seems to be less abundant, but in ion beams from CO and N_2O the ^2P state seems to be equally important. — In collisions between an O^+ ion in the ^2P state and a H_2 molecule, two kinds of charge exchange are energetically possible. The first possibility is that the O^+ ion makes a transition to the atomic state ^3P. Then the RE is 18.64 and H^+ ions are obtained according to process *a* (see Table 3). The other possibility is that the O^+ ion makes a transition to the atomic state ^1D. Here RE is 16.67 and H_2^+ ions are obtained according to process *x* (see Table 2). As the first transition represents a certain violation of the Franck-Condon principle, its probability is small. Since in ion beams from CO and N_2O the ^2P state seems to be of the same importance, the cross-sections for formation of H_2^+ according to the second possibility ought to be equal in the two cases. — From Table 2 it is, however, evident that the cross-section for formation of H_2^+ is considerably larger when using ions from CO than from N_2O. This must indicate that the ion beam from CO contains a great number of ions in the ^2D state with RE 16.94. This state does not seem to be of the same importance for the ions from N_2O and CO_2.

Table 2.

Atomic Ion	Frag-ment	$Q_{\text{Lind-holm}}$	$Q_{25\text{ V}}$ Å²	$Q_{50\text{ V}}$ Å²	$Q_{150\text{ V}}$ Å²	$Q_{400\text{ V}}$ Å²	$Q_{900\text{ V}}$ Å²	RE and author
Ar^{++}	H_2^+	0.15	0.25	0.15	0.10	0.10	0.10	
Kr^{++}		0.15			0.004	0.006	0.009	
He^+		0.030			0.001	0.003	0.030	24.58
Ne^+		0.003					0.005	21.56, 21.66
F^+		2.4		5.4	3.3	2.7	2.4	17.42 x
Ar^+		7.2	6.9	7.2	7.5	9.5	7.5	15.76, 15.94 x
Ar^+			3.0	9.0	14.0	14.0	9.0	Wolf [33]
Ar^+			11.0	17.0	20.0	20.0	15.0	Gilbody-Hasted [11]
Ar^+					14.0	13.0	13.0	Ghosh-Sheridan [15]
Kr^+		0.06	0.002	0.04	0.06	0.15	0.40	All RE below 14.67
N^+		1.5		0.3	0.7	2.1	2.4	All RE below 15.03
N^+			0.3	2.1	1.8	3.0	2.4	Wolf [33]
N^+			1.2	2.1	3.6	5.4	5.4	Gilbody-Hasted [11]
H^+		1.5		0.2	0.3	1.2	4.0	RE 13.60
H^+			1.8	1.5	0.6	2.1	4.5	Wolf [33]
H^+					0.6	2.1	4.5	Stedeford-Hasted [17]
H^+						2.0	4.5	Fite *et al.* [34]
O^+ from CO		3.0		9.0	9.0	9.0	9.0	16.67, 16.94 x
O^+ from N_2O		3.0	4.2	4.5	6.0	8.0	7.0	16.67 x
O^+ from CO_2		1.2	2.4	3.0	4.0	4.0	4.0	16.67 x
C^+		0.2	1.0	1.2	1.4	1.5	1.5	16.58 x
C^+				0.3	1.2	1.8	1.8	Gilbody-Hasted [11]
S^+		0.02		0.04	0.06	0.08	0.08	All RE below 12.20
Cl^+		0.3		0.4	0.5	0.7	0.9	All RE below 14.45
B^+		0.1						All RE below 12.92
Br^+		0.0						All RE below 13.25
H_2^+		7.3		10.9	7.0	4.9	4.9	16.4–17.4 x
H_2^+			7.1	8.5	7.4	5.4	5.1	Wolf [35]
H_2^+			7.9	7.2				Simons *et al.* [36]
H_2^+					7.9	8.1	8.2	Stedeford-Hasted [17]
H_2^+			7.3	12.1	9.1	7.3	7.3	Gilbody-Hasted [11]
H_2^+					7.9	5.8	5.8	Dillon *et al.* [14]
H_2^+					10.6	10.6	10.6	Ghosh-Sheridan [15]
H_2^+						6.5	6.3	Fite *et al.* [34]
CO^+				1.2	2.1	4.0	4.5	16.53 x
N_2^+				8.0	21.0	26.0	26.0	15.58, 16.69 x
N_2^+				9.0	21.0	17.0	15.0	Wolf [33]
N_2^+					21.0	21.0	20.0	Ghosh-Sheridan [15]

IP: x: 16.4–17.4 eV. $H_2 \rightarrow H_2^+ \, ({}^2\Sigma_g^+)$.

H_2^+: RE from about 16.4 to about 17.4 (and possibly from about 13 to 14) eV, which will be discussed in connection with the investigation of H_2.

CO^+: We must assume that the incident CO^+ ions are mainly in the $X\ {}^2\Sigma^+$ state. As the corresponding RE amounts to about 14.0 we expect very small cross-sections in the process $CO^+ + H_2 \rightarrow H_2^+$. The large cross-sections given in Table 2 can therefore hardly be explained in any other manner than by assuming that some CO^+ ions are in the $A\ {}^2\Pi_i$ state with RE 16.53. This assumption is astonishing, since the ions formed in this state in the ion source should have had time to make a transition to the ground state by emission of radiation (Comet-Tail-Bands [30]), during their

Table 3.

Atomic Ion	Fragment	Q_{Lindholm}	$Q_{25\,\mathrm{V}}$ Å^2	$Q_{50\,\mathrm{V}}$ Å^2	$Q_{150\,\mathrm{V}}$ Å^2	$Q_{400\,\mathrm{V}}$ Å^2	$Q_{900\,\mathrm{V}}$ Å^2	RE and author
Ar^{++}	H^+	0.06			0.01	0.02	0.02	
Ar^{++}				2.4	1.5	2.7		Wolf [37]
Kr^{++}		0.015		0.012	0.015	0.018	0.018	
He^+		0.06			0.02	0.03	0.03	*b*
He^+					1.4	1.5	1.2	Stedeford-Hasted [17]
Ne^+		0.02			0.002	0.003	0.003	*a*, *b*
F^+		0.5		0.60	0.45	0.20	0.15	20.01, *a*
Ar^+		0.2		0.006	0.21	0.12	0.04	
Kr^+		0.03			0.005	0.03	0.03	
N^+		0.15					0.06	20.39 is missing
H^+		0.06						
O^+ from CO		0.15		0.50	0.25	0.15	0.05	18.64, *a*
O^+ from N_2O		0.15	0.65	0.45	0.18	0.12	0.05	18.64, *a*
O^+ from CO_2		0.09	0.40	0.30	0.15	0.09	0.04	18.64, *a*
C^+		0.03					0.03	
S^+		—					0.003	
Cl^+		0.03					0.02	
B^+		0.1						
P^+		0.0						
Br^+		0.0						
H_2^+		0.15		0.07	0.06	0.05	0.04	

IP: *a*: 18.05—about 20 eV. $H_2 \rightarrow H_2^+ (^2\Sigma_g^+) \rightarrow H^+ + H$.
b: about 26—about 32 eV. $H_2 \rightarrow H_2^+ (^2\Sigma_u^+) \rightarrow H^+ + H$ with kinetic energy.

passage through the mass spectrometer *A*. From Table 2 is further apparent that the cross-section diminishes when the kinetic energy of the incident ions decreases. The reason may possibly be that the retardation lengthens the transit time so that the radiation can be emitted, and then the ions are in the ground state when they reach the collision chamber. This interpretation agrees with Hasted's [23].

Added in proof: Recently, R. G. Bennett and E. W. Dalby, J. Chem. Phys. *32*, 1111, 1960, have measured the lifetime of the A state as $2.6 \cdot 10^{-6}$ sec, which proves the preceding hypothesis.

N_2^+: The difficulties in interpreting the process $N_2^+ + H_2 \rightarrow H_2^+$ are analogous to the difficulties with the CO^+ ions. The main part of the incident ions probably are in the $X\,^2\Sigma_g^+$ state with RE 15.58, but possibly some ions are in the $A\,^2\Pi_u$ state with RE 16.69. This makes it possible to explain in the same manner as for CO^+ the very large cross-section as well as the decrease of the cross-section with decreasing kinetic energy. This interpretation is supported by the observation by Douglas [31] that the $A\,^2\Pi_u - X\,^2\Sigma_g^+$ bands are remarkably weak, and by measurements by Hasted [23]. (New measurements [32] have shown that, on the other hand, the life time of the $B\,^2\Sigma_u^+$ state is very short.)

The measurements on H_2

The results of the measurements on H_2 are given in Tables 2 and 3. In these the first column gives the incident atomic ions arranged according to their ionization potentials. At the bottom of the tables we have further given the results with some incident molecular ions. The second column gives the measured fragment, H_2^+ and H^+ respectively. The third column gives unpublished measurements which Lindholm obtained in 1954 with the old apparatus. The following columns give the cross-sections for some kinetic energies of the incident atomic ion. (For the doubly charged ions the index does not mean energy but voltage.) The last column gives the RE that is probably responsible for the process in question. The AP for the different processes are given below the tables. The different processes are designed x, a, and b.

The tables also give experimental values obtained by other authors, who are listed in the last column. These measurements were performed without magnetic analysis of the collision products and therefore they have been given in Table 2 or Table 3, respectively, depending upon whether the collision processes can be assumed to take place with the formation of H_2^+ or H^+.

Table 2 shows that the agreement between the earlier measurements and ours usually can be accepted. This is, however, not the case with the results with Ar^{++} and He^+ in Table 3. In these cases Wolf [37] and Stedeford and Hasted [17] respectively have obtained large cross-sections although our values in Tables 2 and 3 are especially small. This will be discussed later on.

Earlier investigations on H_2

The ionization and dissociation of the hydrogen molecule have been the subject of a large number of investigations. Reviews are given by Massey and Burhop [7], Smyth [38], and McDowell [39].

The result of these investigations is that the ionization energy of the H_2 molecule amounts to 15.44 eV. The H_2^+ molecular ion is formed in the ground state $^2\Sigma_g^+$. This process we call process x. The probability for the different transitions in the ionization is, according to the Franck-Condon principle, determined by the form of the potential curves. These are known for H_2 and H_2^+ by theoretical computations [38, 40, 41, 42]. The difference between the internuclear distances in H_2 and H_2^+ is unusually large. The internuclear distance in H_2 is 0.74 Å and in H_2^+ 1.06 Å. Owing to this, higher vibrations are excited to an unsually high degree when H_2^+ is formed from H_2 in the ground state. From the wave functions for H_2^+ it is apparent that the equilibrium internuclear distance for H_2 approximately coincides with the quantum-mechanical turning points of the vibrational states of H_2^+ with quantum numbers between about 4 and 8. In the ionization of H_2, H_2^+ is therefore formed to a large extent with these vibrations excited. This corresponds to transferred energies between 16.4 and 17.1 eV. Although the AP for formation of H_2^+ is 15.44 eV, we must in the following discussion take into consideration that there exists a continuum of ionization energies (IP). This continuum begins at 15.44 eV and extends several eV upwards. The probability for the transition has a broad maximum between the limits, 16.4 to 17.1 eV. For our purposes the domain can be considered as a continuum as the distance between two neighbouring vibrational energies in H_2^+ is of the order of magnitude 0.2 eV. (According to diagrams given by Gilbody and Hasted [11] such an energy defect would correspond to a maximum of the collision cross-section at such low kinetic energies of the incident ions that the curve practically obtains resonance form.) (Recently, Krauss and Kropf [43] have computed the overlap integrals using Morse functions and have found a maximum for the vibrational quantum number 2.

This small number probably depends on the fact that the Morse function does not represent the repulsive portion of the potential energy curve at all well. It seems therefore to be of importance to repeat these computations using the exact potential curve.)

If the absorbed energy is greater than 18.05 eV, the above-mentioned $^2\Sigma_g^+$ state will be formed in a vibrational state that is so highly excited that it lies above the dissociation limit of the molecular ion. It will therefore dissociate so that H^+ ions with a very small kinetic energy are formed. The probability for this process (designated as process *a*), is rather small as it represents a weak violation of the Franck-Condon principle. If the absorbed energy is greater than the limit mentioned above, the energy excess will cause the resulting H^+ ions to have some kinetic energy. The probability for process *a* will then be smaller as the violation of the Franck-Condon principle becomes of more importance and as the kinetic energy of the H^+ ions causes an intensity decrease in the mass-spectrometrical analysis. We therefore have to consider process *a* of importance only in the energy range from 18.05 to about 20 eV.

At high absorbed energies between about 26 eV and about 32 eV a new process, process *b*, takes place. In this process H_2^+ is formed in the repulsive $^2\Sigma_u^+$ state. This dissociates immediately and H^+ ions with a high kinetic energy, 4 eV or more, are obtained. Owing to this kinetic energy it is practically impossible to observe such ions in our mass spectrometer, in which the pole distance amounts to 10 mm and the length of the ion path is about 1000 mm.

Discussion of the measurements on H_2

For the discussion of the collisions between H_2^+ and H_2 we have to begin with the formation of H_2^+. When H_2^+ is formed in the ion source by electron bombardment the absorbed energy usually amounts to between 16.4 and 17.1 eV, according to the preceding discussion, and H_2^+ is formed in a highly excited vibrational state. There is no risk that this ion emits radiation and makes a transition to the vibrational ground state as H_2^+ is a homonuclear molecule. We therefore expect a RE for H_2^+ amounting to between 16.4 and 17.1 eV. There is, however, always some probability that the H_2^+ ion when passing a molecule in the collision chamber may happen to have a large atomic distance. In this case the transition in the charge exchange takes place to an outer part of the potential curve $^1\Sigma_g^+$ for H_2, and RE will be very low (of the order of magnitude 13 eV). — In collisions between H_2^+ and H_2 we expect that process *x* will take place and that the cross-section curves will have resonance form. Further we expect rather small cross-sections owing to the possibility of low RE of the incident ion, and finally we expect, owing to this, a maximum for higher kinetic energies of the incident ion. — The results in Table 2 agree with these expectations although we did not find any maximum. Such a maximum has, however, been observed by Gilbody and Hasted [11] at 2500 eV and possibly also by Stedeford and Hasted [17]. The last mentioned authors explain the reason for the maximum in another manner. The maximum has further been observed by Fite, Brackmann and Snow [34] and by Afrosimov, Il'in and Fedorenko [44].

A result of the discussion is that RE for H_2^+ must necessarily be lower than 18.05 eV, as a molecular ion with higher energy immediately dissociates. It follows that in collision between H_2^+ and H_2 no H^+ ions can be formed according to process *a*. This result agrees with the exceedingly small cross-section we have observed for this reaction (see Table 3). As the cross-sections diminish with increasing kinetic energy of the incident ions, it is evident that the maximum observed by Gilbody and Hasted [11] can hardly be explained by means of process *a*.

In the process $H^+ + H_2 \rightarrow H_2^+$ the cross-sections are small and increase rapidly with the kinetic energy of the incident ions. This result is in good agreement with the measurements by Wolf and by Stedeford and Hasted and must be considered as a support for the idea that the IP-range for process x is considerably higher than 15.44 eV. Stedeford and Hasted [17] point out that the value 15.44 ought to give a maximum at 900 eV while they have found a maximum at about 6000 eV.

The results from bombardments with F^+ and O^+ give further support for the IP-range given above. With F^+ the curve has resonance form, and this must be interpreted as meaning that the IP-range, 16.4 to 17.1 eV, which has been given above, probably is too low. The range must extend past 17.42 eV, which is the RE for F^+. RE 16.94 and RE 16.67 must be inside the range as the cross-sections which are obtained with O^+ ions from CO are large also for low kinetic energies. In this manner we have arrived to the IP-range 16.4 to 17.4 eV given in Table 2. (Recently, Hasted [45] has made use of the IP-range, derived in this paper.)

For Ar^+ the RE are 15.76 and 15.94 eV. As these values lie near the lower limit of the IP-range for H_2, we expect to obtain a maximum on the cross-section curve, and also rather large cross-sections for low kinetic energies. This agrees with our measurements and with the curves by Wolf and by Gilbody and Hasted. In collisions with C^+ the case is the same, although here RE 16.58 is of comparatively small importance in the ion beam.

For Kr^+ (RE 14.67), N^+ (RE 15.03), S^+ (RE 12.20), and Cl^+ (RE 14.45) the cross-sections are small as the RE for these ions are much lower than the IP-range for H_2.

In bombardment with He^+ ions the cross-sections for formation of H_2^+ and H^+ are very small. As mentioned above, Stedeford and Hasted [17] have on the other hand observed rather large cross-sections in our energy range. They explain this by assuming that process *b* takes place. As they do not analyze the collision products magnetically, they can of course observe all H^+ ions that are formed during this process in spite of their kinetic energy, but this is not possible in our mass spectrometer. — The results in bombardment with Ar^{++} can be explained in the same manner.

The measurements on N_2

The results of the measurements on N_2 are given in Tables 4 and 5, which are analogous with Tables 2 and 3. The first column gives the incident ion, the second gives the measured fragment, N_2^+ and N^+, respectively, and the third gives Lindholm's earlier values [4]. The following columns give the cross-sections for some kinetic energies. (For the doubly charged ions the index does not mean energy but voltage.) Finally the last column gives the RE that probably is responsible for the process in question. The different processes are given below the tables. The notations agree with the notations in [4] except regarding the three processes e_1, e_2, and e_3, which correspond to the processes that Frost and McDowell [24] have observed in electron impact. Burns [46] has found a further process at 26.2 eV, which if it exists, cannot change our conclusions.

The tables also give experimental values obtained by other authors. As these are obtained without magnetic analysis of the collision products, they have been given in

Table 4.

Atomic Ion	Fragment	Q_{Lindholm}	$Q_{25\,\text{V}}$ Å²	$Q_{50\,\text{V}}$ Å²	$Q_{150\,\text{V}}$ Å²	$Q_{400\,\text{V}}$ Å²	$Q_{900\,\text{V}}$ Å²	RE and author
Ar^{++}	N_2^+	0.9	0.40	0.40	0.40	0.36	0.33	About 24, *c*
Kr^{++}		0.9		0.2	0.3	0.5	0.7	About 21, *b*
He^+		0.6	0.60	0.45	0.25	0.20	0.20	24,58, *c*
Ne^+		0.3			0.08	0.08	0.08	21.56, 21.66
F^+		15	18	17	12	12	12	17.42,*a*; 20.01, *b*; 22.98, *c*
Ar^+		18	4.2	3.6	3.9	5.2	6.8	15.76, 15.94, *x*, *a*
Ar^+				11.0	15.0	16.5	17.5	Gilbody-Hasted [11]
Ar^+					14.5	16.0	16.5	Ghosh-Sheridan [15]
Kr^+		0.3					0.06	All RE below 14.67
N^+		2.4	1.2	1.2	1.5	1.8	2.1	15.03, *x*
N^+			0.6	2.1	2.1	2.7	3.3	Wolf [33]
N^+			0.4	0.6	0.7			Potter [16]
H^+				0.03	0.3	1.5	4.5	13.60, *x*
H^+					0.6	3	8	Gilbody-Hasted [11]
O^+ from CO		30	18	16	14	13	12	14.98, *x*; 16.67, 16.94, *a*; 18.64, *b*
O^+ from N_2O		12		9.5	8.2	7.9	7.6	16.67, *a*; 18.64, *b*
O^+ from CO_2		6		3.3	3.3	3.6	3.9	16.67, *a*; 18.64, *b*; 13.62, *x*
O^+			4.5	4.5	4.5			Potter [16]
O^+			3.3	3.6	3.6	3.9	3.9	Hasted [10]
C^+		3		3.0	2.7	2.4	2.4	16.58, *a*
S^+		0.4		0.09	0.12	0.15	0.24	All RE below 12.20
H_2^+			9.0	8.5	7.5	6.0	6.0	16.4–17.4, *a*
H_2^+			5.8	7.6	6.7	6.7	7.6	Wolf [33]
H_2^+					9.7	11.3	15.2	Ghosh-Sheridan [15]
N_2^+		27		36	30	27	23	15.58, *x*; 16.69, *a*
N_2^+			18	20	22	19	18	Wolf [35]
N_2^+			25	24	22			Potter [16]
N_2^+				27	24	19	15	Dillon *et al.* [14]
N_2^+					27	26	26	Ghosh-Sheridan [15]

AP: *x*: 15.576 Ionization with formation of $N_2^+ \; X \; {}^2\Sigma_g^+$.
a: 16.694 Ionization with formation of $N_2^+ \; A \; {}^2\Pi_u$.
b: 18.746 Ionization with formation of $N_2^+ \; B \; {}^2\Sigma_u^+$.
c: 23.586 Ionization with formation of $N_2^+ \; C \; {}^2\Sigma_u^+$.

Table 4 or Table 5, respectively, depending on whether the collision processes can be assumed to take place with formation of N_2^+ or N^+.

Table 4 shows that the agreement between the earlier measurements and ours can be accepted. This is, however, not the case with the results for He^+ and Ne^+ in Table 5, for which Wolf [47] has obtained considerably larger collision cross-sections. The agreement as to the dependence of the kinetic energy is, however, rather good.

A comparison with the earlier measurements by Lindholm [4] shows, that the new cross-sections for formation of N^+ are much smaller than these (see Table 5). The cause of this is probably the use of magnetic scanning instead of the electrostatic scanning used earlier.

Earlier investigations on N_2

A review of the structure and dissociation of the nitrogen molecule has been given by Lindholm [4]. Detailed reviews have also been given by McDowell [39], and Frost

Table 5.

Atomic Ion	Fragment	Q_{Lindholm}	$Q_{25\,\text{V}}$ Å^2	$Q_{50\,\text{V}}$ Å^2	$Q_{150\,\text{V}}$ Å^2	$Q_{400\,\text{V}}$ Å^2	$Q_{900\,\text{V}}$ Å^2	RE and author
Ar^{++}	N^+	6	0.30	0.36	0.45	0.60	0.63	About 24, e_1
Kr^{++}		1.8		0.06	0.12	0.21	0.30	About 21, e_1
He^+		12	2.6	2.0	1.4	1.0	0.8	24.58, e_1
He^+				6.7	6.1	5.5	5.1	Wolf [47]
Ne^+		6		0.2	0.3	0.4	0.4	21.56, 21,66, e_1
Ne^+				0.3	2.4	3.0	3.6	Wolf [47]
F^+		6		0.2	0.4	0.5	0.6	22.98, e_1
Ar^+		0.6		0.03	0.04	0.06	0.08	
Kr^+		0.3				0.006	0.009	
N^+		0.6			0.12	0.15	0.18	
H^+							0.05	
O^+ from CO		1.8					0.2	
O^+ from N_2O		0.9					0.06	
O^+ from CO_2		0.9		0.04	0.04	0.05	0.05	
C^+		0.6					0.02	
S^+		0.1					0	
H_2^+				0.003	0.02	0.08	0.13	
N_2^+		0.6		0.04	0.04	0.05	0.08	

AP: e_1: $N_2 + 24.30\ \text{eV} \rightarrow N^+\ (^3P) + N\ (^4S)$.
e_2: $N_2 + 26.68\ \text{eV} \rightarrow N^+\ (^3P) + N\ (^2D)$.
e_3: $N_2 + 27.87\ \text{eV} \rightarrow N^+\ (^3P) + N\ (^2P)$.

and McDowell [24, 48], Mulliken [49] and Fineman and Petrocelli [25, 26]. Since Lindholm's paper progress has, however, been made in the study of the molecule.

In the first place it seems now to be definitively proven by the analysis of the band spectrum of NO by Lagerqvist and Miescher [50] that the dissociation energy of nitrogen amounts to 9.76 eV. Several earlier investigations had supported this value [27, 24, 51, 52].

Further, the N_2 molecule has been thoroughly investigated by the retarding potential difference method by Fox and Hickam [53]. They have observed two higher AP corresponding to transitions to the states $A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$ which earlier could only be observed spectroscopically. Later Frost and McDowell [48] have made more detailed investigations with the same method and have been able to observe also transitions to $C\ ^2\Sigma_u^+$ mass-spectrometrically. It is interesting that Frost and McDowell's curve shows a large probability for the transition to the C state, although this state has been formed by simultaneous ionization of one electron and excitation of another.

Finally Frost and McDowell [24] and Fineman and Petrocelli [25, 26] have investigated the formation of N^+ in electron impact by the same method.

Discussion of the new measurements on N_2

For the process $H^+ + N_2 \rightarrow N_2^+$ the energy defect amounts to 2 eV. This process has been investigated earlier and discussed by Gilbody and Hasted [11]. Table 4 shows that the cross-section diminishes very quickly with decreasing kinetic energy of the incident ion, which indicates that here we have process x. Carleton [54] and

Carleton and Lawrence [55] have shown that the processes *a* and *b* also take place at higher energies but their cross-sections seem to be rather small.

For the process $Ar^+ + N_2 \rightarrow N_2^+$ the cross-section curve has a weak minimum contrary to the other collision processes. This must signify that we have two processes, *x* and *a*. The first corresponds to the resonance case with maximum for zero kinetic energy, and the second corresponds to an energy deficit with maximum for higher kinetic energies. The reason why process *x* seems to be of small importance may possibly be explained by the comparatively small probability for process *x* that Frost and McDowell [48] have observed in electron impact.

For the process $O^+ + N_2 \rightarrow N_2^+$ the results are quite different depending on the origin of the O^+ ions. This supports our conclusions from the investigations with H_2. The ion beam obtained with CO contains a large number of ions in the ^2P-state with RE 18.64, 16.67, and 14.45 eV, and also a large number of ions in the ^2D-state with RE 16.94 and 14.98. Therefore the cross-sections are large and the curve has resonance form. The ion beam obtained with N_2O contains the same number of ions in the ^2P-state, but only a few ions in the ^2D-state and the cross-sections are smaller. The ion beam obtained with CO_2 contains ions mainly in the ^4S-state with RE 13.62 eV and further a certain number of ions in the ^2P-state. Therefore the cross-sections are small and the curve has defect form.

The interpretation of the process $N^+ + N_2 \rightarrow N_2^+$ is complicated by our earlier result that the incident N_2^+ ions seem to be partly in the $A\,^2\Pi_u$-state. We thus obtain two RE, 15.58 and 16.69 eV. Both of these possibilities give, however, resonance form and the conclusion by Potter [16] that the ion beam should consist of only $X\,^2\Sigma_g^+$ ions, seems therefore not justified. Another complication is that the ions that leave the ion source might be in higher vibrational states. This seems, however, not to be the case according to measurements by Frost and McDowell [48]. We thus expect large cross-sections and resonance form for this collision process, which agrees with the measurements given in Table 4.

When N_2^+ ions are obtained by bombarding with Kr^+ and S^+ the cross-sections are small owing to low RE. When bombarding with N^+ the curve has defect form. With H_2^+ mainly process *a* takes place, but possibly also process *x*. With F^+ the cross-sections are very large, as all three processes *a*, *b*, and *c* are possible.

According to Table 5 the cross-sections usually are small for formation of N^+. As mentioned above, the cross-sections are small both in comparison with Wolf's and with Lindholm's measurements. In the following discussions we have, however, only use for the relative magnitude of the cross-sections and their dependence on the kinetic energy of the incident ions. We limit the discussion to Ne^+ and He^+.

We see in Table 4 that for the process $Ne^+ + N_2 \rightarrow N_2^+$ the cross-sections are very small. This shows that the probability for formation of the $C\,^2\Sigma_u^+$ state is unimportant, owing to the difference between RE 21.6 and AP 23.6. Further, it is clear that there is very small probability for formation of the $B\,^2\Sigma_u^+$ state with simultaneous strong excitation of the vibrations, since the internuclear distances in N_2 and in the B state of N_2^+ is almost the same [56, 48].

For the process $Ne^+ + N_2 \rightarrow N^+$ the curve has defect form. This agrees well with the assumption that RE is 21.6 and AP is 24.3. — Lindholm [4] found a rather large cross-section for this process, which he interpreted as indicating an AP of 21.914 eV, and considered as a support for the lower dissociation energy for N_2, 7.37 eV, which had earlier been discussed by several investigators. The cause for this result was that Lindholm had no possibility to investigate the cross-sections as a function of the kinetic energy of the ions. After the new measurements it now seems to be necessary to abandon Lindholm's interpretation.

When N_2^+ and N^+ are formed in collisions with He^+, in both cases the cross-section curve has resonance form and the cross-sections are larger than the corresponding ones with Ne^+. As transitions to the $B\ ^2\Sigma_u^+$ state can be neglected in a higher degree than with Ne^+, the explanation must be a transition to the $C\ ^2\Sigma_u^+$ state or to one of the more or less repulsive or slightly attractive states with dissociation energy 24.30 eV ($^2\Pi_g$, $^4\Sigma_g^-$, $^4\Sigma_u^+$, $^4\Pi_g$, $^4\Pi_u$, $^6\Sigma_g^+$, $^6\Sigma_u^+$, $^6\Pi_g$, $^6\Pi_u$) [49, 57, 58]. In the former case we observe formation of N_2^+ and in the latter case formation of N^+ (cf. [59, 39, and 57]). If N^+ is produced using higher energy than 24.30 eV we therefore expect that the ions have initial energy. This agrees with measurements by Kandel [60] and Hagstrum [61].

The new measurements with He^+ are a further support for the discussion by Lindholm [4] of the excitation methods that have been used in the spectroscopic investigations of N_2^+. It has appeared that when using a discharge through helium containing a trace of nitrogen, the N_2^+ bands are strong compared with the N_2 bands. Douglas [59] and Wilkinson [57] have tried to explain this by assuming that the discharge tube contains a large number of nitrogen ions and atoms, and they further assume that N_2^+ has been formed by inverse predissociation when an N^+ ion and an N atom come together. — Lindholm agreed with this explanation and pointed out that his measurements showed that the discharge tube contains large quantities of N atoms and N^+ ions. The weak point in Lindholm's proof was that his measurements were performed with a kinetic energy of 500 eV for the incident ion, and in the discharge tube the energies probably are much lower. However, the new measurements show clearly that for very low energies the cross-sections are very large for formation of N and N^+.

Lindholm [4] finally discussed the spectrum which is obtained from a discharge tube with Ne containing traces of N_2, and he was of the opinion that also in this case the explanation must be founded on the assumption that the discharge tube contains large numbers of N atoms and N^+ ions. The new measurements show, however, that this explanation must be erroneous. For the low kinetic energies in the discharge tube the cross-section for formation of N^+ ions in collision with Ne^+ is according to Table 5 very small.

The measurements on CO

The results of the measurements on CO are given in Tables 6, 7, and 8. The first column lists the incident ions and the second gives the measured fragment; CO^+, O^+, and C^+, respectively. The third column gives Lindholm's earlier values [5]. The following columns give the collision cross-sections for some kinetic energies. (For the doubly charged ions the index does not mean energy but voltage.) The last column finally gives the RE that probably is responsible for the process in question. The different processes are given below the tables.

Table 6 further gives values measured by other authors, which were obtained without magnetic analysis of the collision products. The agreement is considered acceptable.

A comparison with the earlier measurements by Lindholm [5] shows that the new cross-sections for formation of C^+ and O^+ are much smaller. The reason for this is the electrostatic scanning previously used by Lindholm.

Table 6.

Atomic Ion	Frag-ment	$Q_{\text{Lind-holm}}$	$Q_{25\,\text{V}}$ Å²	$Q_{50\,\text{V}}$ Å²	$Q_{150\,\text{V}}$ Å²	$Q_{400\,\text{V}}$ Å²	$Q_{900\,\text{V}}$ Å²	RE and author
Ar^{++}	CO^+	0.3		0.27	0.27	0.30	0.36	About 24
Kr^{++}		4.5	1.5	1.7	2.3	2.6	2.7	About 21, *b*
He^+		0.6		0.09	0.11	0.14	0.18	24.58
Ne^+		0.24	0.21	0.18	0.12	0.12	0.15	21.56, 21.66
F^+		45	23	20	15	14	15	17.42, *a*; 20.01, *b*
Ar^+		4.5		1.0	2.0	2.7	3.0	15.76, 15.94, *a*
Kr^+		12		17	15	12	10	14.00, 14.67, *x*
N^+		15	8.5	9	10	12	14	Mostly 14.54, *x*. Only a little 14.06, *x*
H^+			5	8	20	18	17	13.60, *x*
H^+			5	8	18	27	27	Gilbody-Hasted [11]
O^+ from CO		40						
O^+ from N_2O		40		18	18	21	24	13.62, *x*, and *a* little 16.67, *a*, and 14.45, *x*
O^+ from CO_2		40		14	15	18	24	13.62, *x*
C^+		3		6	4	3	3	16.58, *a*
S^+		0.6		0.7	0.7	0.8	0.9	All RE below 12.20
Cl^+			1.8	1.8	2.0	2.4	3.7	14.45, 14.34, *x*
B^+		4.5				1.2	1.8	12.92, *x*
H_2^+				20	17	15	14	16.4–17.4, *a*. Possibly 13–14, *x*
CO^+			45	37	29	27	25	14.00, *x*; 16.53, *a*
CO^+				33	27	21	15	Dillon *et al.* [14]
N_2^+			8.0	8.0	8.3	8.6	8.9	16.69, *a*; 15.58, *x*

AP: *x*: 14.009 Ionization with formation of CO^+ $X\ {}^2\Sigma^+$.
a: 16.532 Ionization with formation of CO^+ $A\ {}^2\Pi_i$.
b: 19.670 Ionization with formation of CO^+ $B\ {}^2\Sigma^+$.

Table 7.

Atomic Ion	Frag-ment	$Q_{\text{Lind-holm}}$	$Q_{25\,\text{V}}$ Å²	$Q_{50\,\text{V}}$ Å²	$Q_{150\,\text{V}}$ Å²	$Q_{400\,\text{V}}$ Å²	$Q_{900\,\text{V}}$ Å²	RE and author
Ar^{++}	O^+	0.2					0	
He^+		1			0.12	0.09	0.09	24.58, *g*
Ne^+		0.3	0.027	0.030	0.030	0.030	0.030	
F^+							0.3	
N^+ from N_2		0.1		0.4	0.6	0.7	0.7	N_2^{++}?
H^+							0	
O^+ from CO_2							0	
C^+							0	
Cl^+							0.05	
B^+							0.03	
H_2^+							0.02	
CO^+		0.03				0.02	0.1	

AP: *g*: $CO + 24.73\ \text{eV} \rightarrow C\ ({}^3P) + O^+\ ({}^4S)$.

Table 8.

Atomic Ion	Fragment	Q_{Lindholm}	$Q_{25\text{ V}}$ Å^2	$Q_{50\text{ V}}$ Å^2	$Q_{150\text{ V}}$ Å^2	$Q_{400\text{ V}}$ Å^2	$Q_{900\text{ V}}$ Å^2	RE and author
Ar^{++}	C^+	3		1.1	0.9	0.8	0.7	About 24, d_2
Kr^{++}		5	0.2	0.2	0.3	0.5	0.5	About 21, d_1
He^+		9	1.7	1.4	0.8	0.6	0.4	24.58, d_2
Ne^+		3	0.8	0.7	0.6	0.5	0.4	21.56, 21.66, d_1?
F^+		9					0.4	
Ar^+		2		0.06	0.09	0.15	0.18	
N^+		1			0.5	0.3	0.2	N_2^{++}?
H^+							0.05	
O^+ from CO		3						
O^+ from N_2O		3			0.4	0.3	0.3	
O^+ from CO_2		3			0.3	0.2	0.2	
C^+		0.6			0.15	0.12	0.06	
Cl^+		0.6					0.06	
B^+		0.2					0.03	
H_2^+			0.04	0.06	0.09	0.15	0.18	
CO^+		1.2		0.18	0.15	0.12	0.12	

AP: d_1: $CO + 22.37\text{ eV} \rightarrow C^+ (^2P) + O (^3P)$.
d_2: $CO + 24.34\text{ eV} \rightarrow C^+ (^2P) + O (^1D)$.
d_3: $CO + 26.56\text{ eV} \rightarrow C^+ (^2P) + O (^1S)$.

Earlier investigations on CO

A review of the structure and dissociation of the CO molecule has been given by Lindholm [5]. This review was founded on the detailed mass-spectrometrical investigation that had been performed by Hagstrum [61]. The situation has, however, changed since then, owing to new investigations.

Branscomb and Smith [62] showed that the electron affinity for oxygen amounts to only 1.48 eV, which value is considerably lower than the earlier accepted value, 2.2 eV [27]. Further, they were able to show that the negative oxygen ion probably lacks any excited state. As a consequence of this work, Hagstrum [51] gave a reinterpretation of his mass-spectrometrical measurements. Although this somewhat impaired the agreement between Hagstrum's measurements and interpretations it now seems necessary to start from this new interpretation. This means that we must assume as correct the value 11.111 eV for the dissociation energy of CO.

At the same time Lagergren [63] made a thorough investigation of the mass spectrum of CO. He had the same difficulties as Hagstrum in interpreting the AP for formation of C^+ at 22.37 eV (our process d_1) and suggested that this fragment is formed from an excited molecule and not from a molecular ion. This means, however, that it should be impossible using charge exchange to obtain C^+ ions at these energies, and his conclusion is therefore in complete disagreement with our measurements as we obtain rather large cross-sections for formation of C^+ using He^+ and Ne^+.

Later, Fineman, Petrocelli, and Daignault [64] and Petrocelli [26] investigated the molecule in a Lozier apparatus. Petrocelli found the AP for formation of C^+ to be 22.57 eV, which is within experimental error of the calculated value of 22.37 eV. Petrocelli was also able to observe O^+ ions in our process g.

Further support for Hagstrum's reinterpretation is the determination of the dissociation energy for NO by Lagerqvist and Miescher [50] with band-spectroscopic methods. A detailed account of these problems is given by Field and Franklin [27].

The AP which correspond to the new interpretations are given below the tables. The processes given below Table 6 are identical with those in Lindholm's paper, but the processes in Tables 7 and 8 agree instead with [26] and [51]. Below Table 8 some possibilities corresponding to excited fragments have been given.

Besides the dissociation processes given in the tables there are two others which are of importance in ion sources in mass spectrometers:

$$\mathrm{CO} + 20.9\ \mathrm{eV} \rightarrow \mathrm{C}^{+}(^{2}P) + \mathrm{O}^{-}(^{2}P) \qquad (\mathrm{e}_1)$$

$$\mathrm{CO} + 23.4\ \mathrm{eV} \rightarrow \mathrm{C}^{-}(^{4}S) + \mathrm{O}^{+}(^{4}S) \qquad (\mathrm{e}_2)$$

As in this case it is a neutral CO molecule which dissociates, these processes are without interest for the present investigation.

Discussion of the new measurements on CO

Process x (AP 14.009) seems to be responsible for the large collision cross-sections for formation of CO^+ in collisions with Kr^+. The curve has resonance form as one RE for Kr^+ is 14.00 and as the internuclear distances in CO and CO^+ in their ground states are practically identical (1.13 Å and 1.12 Å, respectively) [56]. It is remarkable that the curve form is already changed for such a small deviation from energy resonance as 0.4 eV. This is evident from the measurements with N^+ (RE 14.54), H^+ (RE 13.60), O^+ (RE 13.62 and higher), and Cl^+ (RE 14.34 and 14.45), where the curve has defect form. To explain the results with H^+, Gilbody and Hasted [11] have discussed the importance of process a and process b for higher kinetic energies. In collisions with Ar^+ (RE 15.76 and 15.94) the cross-section for formation of CO^+ is small and the curve has defect form. The probability for process x is probably very small owing to the Franck-Condon principle, and therefore it seems to be necessary to explain the cross-sections with Ar^+ by means of process a, which has already been pointed out by Lindholm [5].

Process a (AP 16.532) seems to be responsible for the collision cross-sections for formation of CO^+ in collisions with C^+ (RE 16.58). This curve has resonance form.

Process b (AP 19.670) is, together with process a, responsible for the large cross-sections for formation of CO^+ in collision with F^+ (RE 20.01 and 17.42, respectively), which has already been discussed by Lindholm. We can now add that the curve has resonance form, which supports Lindholm's interpretation. As the $B\,^2\Sigma^+$ state has approximately the same internuclear distance as the $X\,^2\Sigma^+$ state the transition probability will decrease rapidly with increasing RE. This explains the small cross-sections in Table 6 for formation of CO^+ in collisions with Ne^+. With Kr^{++} the cross-sections in this table are considerably larger. von Koch and Lindholm [22] have found that in collisions with C_2H_5OH the effective RE of Kr^{++} in this apparatus amounts to about 21 eV. If we assume that the effective RE of Kr^{++} in collisions with CO is a little lower than the RE of Ne^+ this explains the larger cross-sections with Kr^{++}. Using He^+ (RE 24.58) and Ar^{++} (RE about 24) the cross-sections are small. Whether the transitions in these cases are due to process b or go to some higher unknown state is uncertain.

The formation of O^+ is assumed to take place in process g. All cross-sections are small. With He^+ the resonance is practically perfect (RE 24.58 and AP 24.73), and from Table 7 we see that the curve has a weak resonance form.

The formation of C^+ is of great interest. First we observe that He^+ and Ar^{++} give large cross-sections as their RE approximately agree with the AP 24.34 of process d_2. With Kr^{++} the cross-sections are small and the curve has defect form as its effective RE is low compared with AP 22.37 of process d_1.

In collisions with Ne^+ the cross-section for formation of C^+ is relatively large and the curve has resonance form. This result has been thoroughly checked. The measurements on CO were extended over 4 months, and the collision processes with Ne^+ were investigated several times at the beginning, in the middle, and at the end of this time. The calibration of the apparatus changed somewhat during this time, so that the absolute value of the cross-sections changed with 40 per cent but the curve form was the same at all times. It seems therefore improbable that the result depends on erroneous adjustment of the apparatus. An investigation of the dependence of the cross-sections on the pressure in the collision chamber proved that the effect is not caused by C^+ ions that have been ejected from the graphite on the walls in the collision chamber by the Ne^+ ions. — After the measurements had been finished, the suspicion arose that perhaps the CO gas was not pure. As a mass spectrometric analysis revealed a small impurity of $Fe(CO)_5$ we feared that the C^+ peak might be due mainly to the impurity and postponed therefore the publication of this paper. — Recently the apparatus has been moved from Gothenburg to Stockholm and is now equipped with a recorder. The influence of the impurity can now easily be observed if peak 56 (Fe^+) is recorded simultaneously with peaks 12, 16, and 28. When cooling the inlet system with liquid air peak 56 disappeared but the other peaks remained unchanged. This shows that peak 12 is due entirely to the CO and we feel convinced that our measurements are correct.

Our measurements thus agree with the earlier result by Lindholm [5], which he interpreted as a proof that the AP in question is lower than RE 21.56 and 21.66 for Ne^+. Thus it seemed possible by these measurements to contribute to the discussion of the dissociation energy of CO.

Now that the question regarding the dissociation energy for CO seems to be settled, it is of interest to see to what extent the measurements agree with the theoretical expectations. It is then evident that we could hardly expect resonance form of the curve if the RE amount to 21.56 and 21.66 while the AP amounts to 22.37. Although this energy deficit is considerably smaller than the deficit that Lindholm discussed on the basis of Hagstrum's measurements, it seems too great to explain the form of the curve. The theoretical curve form corresponding to the energy defect $\Delta E = 22.37 - 21.66 = 0.71$ eV, can easily be computed by means of the diagrams given by Gilbody and Hasted [11]. As the mass of the incident ion is 20, we obtain $m^{1/2}\,\Delta E = 3.1$ and $V_{\max} = 3000$ eV. We should therefore expect theoretically that the curve should rise within the whole of our energy range. If finally the experimental AP [61, 63, 26] are taken into consideration the energy deficit will be still larger.

Neither can the explanation be that there exist higher metastable levels in Ne^+. Lindholm [4, 5] has already pointed out that such levels are absent, and Hagstrum [21] has been able to prove this experimentally.

The only possible explanation seems therefore to be that the empirical diagrams given by Gilbody and Hasted are not quantitatively valid for this case. As these diagrams have been obtained from experimental investigations of charge exchange in a number of simple cases (atoms, homonuclear diatomic molecules) without immediate dissociation and without mass-spectrometrical analysis of the secondary ions, it seems to be desirable to check the diagrams using our measurement (cf. [45]). Only the following case is of interest in this connection. — According to Table 5 mainly N^+ is formed in the collisions between Ne^+ and N_2. The cross-section curve from our measurements and from the measurements by Wolf [47] is fairly constant between 400 eV and 900 eV. As the energy defect $\Delta E = 24.30 - 21.66 = 2.64$ eV, $m^{1/2} \Delta E = 11.8$ and $V_{\max} = 40{,}000$ eV. The computed energy of the maximum is thus much higher than the observed. — From this it follows that the explanation of our difficulties in interpreting the formation of C^+ in collisions between Ne^+ and CO is probably that in this case our cross-section curve has a maximum at an energy lower than the range of our measurements.

In collisions with Ar^+ Lindholm obtained surprisingly large cross-sections for formation of C^+. He interpreted these by means of a secondary process which had already been investigated by Hogness and Harkness [65]. Lindholm investigated the process by observation of its pressure dependence. In the new apparatus it has, however, been impossible to observe this process.

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